Generalised mathematical model to estimate Zn, Pb, Cd, Ni, Cu, Cr and As release from contaminated estuarine sediment using pH-static leaching tests

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Highlights (3 to 5 bullet points, maximum 85 characters, including spaces)

- Trace element time-dependent release based on first order series reactions.
- The model fits initial delay of Zn, Pb, Cd and Cu and adsorption of As and Cr.
- The model is valid when applied to sediments with different levels of oxidation.
- Prediction of time-dependent leaching behaviour in scenarios of acidification.

Keywords:

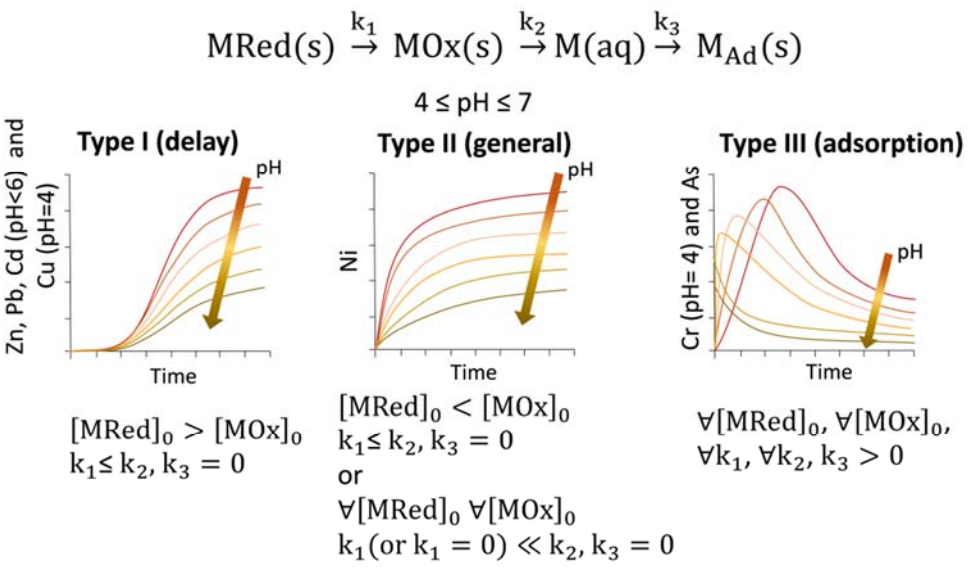
Pollutant release; Modelling; pH-static leaching; Sediment; Acidification; Reactions in series

Abstract

Variations in the environmental conditions in marine and estuarine environments can lead to the release of elements from the sediment to the seawater phase. The pH dependence leaching test with continuous pH-control evaluates the release of constituents as a function of the pH. In this work, analysis of the Zn, Pb, Cd, Ni, Cu, Cr and As release from marine sediment of the Suances estuary (northern Spain) is performed using a

leaching test with continuous pH control at pH values of 4, 5, 5.5, 6, 6.5 and 7 with seawater as the leaching liquid. These pollutants present different experimental leaching patterns over time but not all of them are well fitted by the previous models. Hence, a generalised model of the different time-dependent releases under these conditions is proposed. The model considers three reactions in series: (i) the oxidation reaction of the reduced fraction to consider the speciation change over time, (ii) the metal release of the oxidised fraction to the bulk dissolution and (iii) the adsorption or precipitation after the element release. The maximum concentration of each pollutant that could be released from the reduced fraction and from the oxidised fraction and the rate coefficients are the parameters of the proposed model. The rate coefficients of the reactions for each pollutant fit well to a second order equation as a function of pH. Using the Aspen Custom Modeler software, the model parameters have been estimated. A good agreement between the experimental and modelled concentration values is obtained. In addition to improving upon the previous results from models with reactions in parallel, the proposed model predicts the metal mobility delay at short times for Zn, Pb, Cd and Cu and the adsorption or precipitation process after an initial rapid release (As and Cr) reasonably well. The model provides good results when applied to two sediments with different levels of oxidation. The obtained model parameters would be useful when predicting the release of the studied elements for cases in which polluted sediment is totally mixed with inorganic acid-acidified seawater under continuous pH control semibatch leaching tests.

Graphical abstract



1. INTRODUCTION

Carbon dioxide (CO_2) storage in sub-seabed geological formations is a possible strategy for decreasing the quantity of atmospheric CO_2 (IPCC, 2014). Potential repositories include depleted oil and gas reservoirs, saline aquifers, coal beds and ocean storage. The projects with the highest total CO_2 storage estimates are offshore (Hosa et al., 2011). In the case of ocean storage technology, CO_2 is injected at a great depth, and most of it would remain isolated from the atmosphere for centuries (IPCC, 2005). However, one of its main risks is the potential leakages of direct CO_2 gas and/or CO_2 dissolved in salt water (seawater or the formation's water) which provoke a decrease in the ocean pH value. This acidification could mobilise elements from marine and estuarine sediments (Rodríguez-Romero et al., 2014; Zheng et al., 2012). The risk of potential contaminant release from sediment is usually assessed using leaching tests (Ho et al., 2012; Martín-Torre et al., 2014; Payán et al., 2012a). The mobility and availability of contaminants from a sediment

matrix are highly dependent on the leaching pH (Coz et al., 2007), so pH dependence leaching tests are essential for analysing the importance of these parameters. The pH dependence leaching test with continuous pH-control (CEN/TS 14997, 2006) evaluates the release of constituents as a function of the pH as well as of the buffering capacity of the solid sample (Cappuyns and Swennen, 2005; Centioli et al., 2008; Horckmans et al., 2007; Shtiza et al., 2009).

In consequence, the modelling of experimental pollutant release as a function of time and pH during the leaching test is useful in predicting sediment behaviour under different scenarios. Schwarz et al. (1999) proposed a mathematical model that has been widely used to model the release of elements from soil, sediment and waste subjected to pH dependence leaching tests (Cappuyns et al., 2004a, b; Cappuyns and Swennen, 2008a, b; Ganne et al., 2006; Ho et al., 2012; Van Herreweghe et al., 2012). This model is based on two independent first order kinetic reactions of the two fractions of the sediment. The kinetic reactions have different reaction rates depending on the sediment element partitioning. The element release results obtained using this model have been considered useful for predicting the risk of species release from sediments. Cappuyns and Swennen (2006) modified this model in order to fit experimental results considering an additional sediment fraction consisting of the element not released during the pH-static assay; this new fraction can be defined as the difference between the total concentration of the element under study and the concentration released from the two considered fractions according to the model of Schwarz et al. (1999).

Ho et al. (2012) summarises the four types of leaching behaviour that fit to the model of two independent kinetic reactions proposed by Schwarz et al. (1999): a very rapid element

91 release at the beginning of the experiment, with equilibrium nearly reached after some
92 hours; an initial rapid release followed by a slow release in the final stage of the assay;
93 an initial rapid release followed by a slow but substantial increase until the end of the
94 leaching test; a slow release with equilibrium not achieved at the end of the experiment,
95 but equilibrium conditions would be achieved at longer times. These four behaviours
96 could be considered to be one because the curve pattern is similar; only the slopes are
97 different because of the different rate coefficients corresponding to the kinetic reactions
98 that occur in each fraction of the sediment. The model of Schwarz et al. (1999) interprets
99 these behaviours well. However, this mathematical model is neither suitable to explain
100 the release of elements which starts after a certain period of time, nor the elements that
101 are adsorbed or precipitated after an initial release (Ho et al., 2012). Examples of these
102 behaviours are commonly found in the release of Arsenic (As) (Cappuyns et al., 2004a;
103 Cappuyns and Swennen, 2005) and in the release of Cadmium (Cd) and Zinc (Zn)
104 especially when anoxic sediment and acidic pH values are studied (Cappuyns et al.,
105 2004b; Cappuyns and Swennen, 2005; Ho et al., 2012).
106
107 Previous studies by our research group modelled the release of contaminants from
108 polluted sediment in contact with natural and acidified seawater in batch tests experiments
109 without pH control (batch contact) using geochemical models (Martín-Torre et al., 2015;
110 Payán et al, 2012a, b). Likewise, modelling of the cumulative release of pollutants from
111 column leaching tests as a function of the L/S ratio and pH (Payán et al., 2012a) and the
112 release of Pb and Zn in a column test by a dynamic kinetic model (Payán et al., 2013)
113 have been performed. In the present work, we propose a mathematical model to interpret
114 the release of pollutants from contaminated sediment over time as a function of pH for
115 the pH dependence leaching test with continuous pH control (semibatch contact)

(CEN/TS 14997, 2006). The authors hypothesize that the release of metals is governed by three first order processes in series: oxidation, dissolution and removal from the aqueous phase (precipitation/sorption). A good fit of the model to the experimental results would be useful for obtaining the kinetic constants and predicting the metals release under different pH and redox conditions. The aim of this article is to develop a new generalised kinetic mathematical model that allows estimation of the kinetic constants of the hypothesised release mechanism of Zn, Pb, Cd, Ni, Cu, Cr and As from contaminated marine sediment as a function of the pH during the pH-static leaching test with continuous pH control. Contrary to the model of Schwarz et al. (1999), which considers two independent reactions of first order, we propose three first order reactions in series to explain the three different release patterns obtained. Thus, the model considers the oxidation process or speciation change over time as a possible explanation for the initial delay in the element release as well as the adsorption or precipitation of the pollutant after an initial release by the inclusion of a third reaction of first order. The corresponding kinetic parameters are obtained that allow the simulation of the release of the studied elements at the pH values of 4, 5, 5.5, 6, 6.5 and 7 and with seawater as leaching liquid.

2. KINETIC MODELLING

The pH dependence leaching test with continuous pH control allows study of element release from sediment, soil and waste as a function of pH and time. pH dependence leaching tests can be useful for simulating worst-case scenarios where acidified seawater is in contact with recent sediment under total mixed conditions (Martín-Torre et al., 2015). Therefore, modelling the results of this test is of interest for analysing the evolution of contaminant release over time at different pH values of interest. It is known that element release from soil and sediment is the consequence of many and complex chemical reactions. However, simplified kinetic models, useful in engineering, are usually proposed. These models employ general reaction schemes to interpret the contaminant release.

In this article, a new kinetic model is presented that considers the oxidation process and the adsorption or precipitation processes over time. The proposed model considers that the element (M) is associated with an oxidised fraction of the sediment (MOx) and with a reduced fraction of the sediment (MRed) that must be oxidised or undergo a speciation change before the release of the element. It also considers a possible adsorption or precipitation of the released element through a third reaction in series. The reaction scheme and mass balances of the proposed model, considering first order kinetics are shown in Eqs. 1-5.

$$\mathrm{MRed(s)} \overset{k_1}{\rightarrow} \mathrm{MOx(s)} \overset{k_2}{\rightarrow} \mathrm{M(aq)} \overset{k_3}{\rightarrow} \mathrm{M_{Ad}(s)} \quad (1)$$

$$\frac{d[\mathrm{MRed}]_i}{dt} = -k_{1,i}\,[\mathrm{MRed}]_i \quad (2)$$

$$\frac{d[\mathrm{MOx}]_i}{dt} = k_{1,i}\,[\mathrm{MRed}]_i - k_{2,i}\,[\mathrm{MOx}]_i \quad (3)$$

$$\frac{d[M]_i}{dt} = k_{2,i}\,[MOx]_i - k_{3,i}\,[M]_i \quad (4)$$

$$\frac{d[M_{Ad}]_i}{dt} = k_{3,i}\,[M]_i \quad (5)$$

where $[MRed]_i$, $[MOx]_i$, $[M]_i$ and $[MAd]_i$ are the concentrations of the element i in the reduced sediment fraction, the oxidised sediment fraction, the leaching liquid and in the adsorbed or precipitated fraction, respectively; k_1, k_2 and k_3 are the rate coefficients of the oxidation or change speciation, release reaction and adsorption or precipitation reaction, respectively, and t is the reaction time.

Considering $[M]_{i,0}$ as the initial concentration of the element i in the liquid and $[MRed]_{i,0}$ and $[MOx]_{i,0}$ as the maximum concentration of element i that can be released from the reduced and oxidised fractions of the sediment respectively, the integral of the previous set of differential equations (Eqs. 1-5) is shown in Eq. 6.

$$\begin{aligned}\frac{LS}{1000}\,[M]_i = &\left(\frac{k_{1,i}\,k_{2,i}\,[MRed]_{i,0}}{(k_{2,i}-k_{1,i})\,(k_{3,i}-k_{1,i})}\right)\exp(-k_{1,i}t)\\ &+\left(\frac{k_{1,i}\,k_{2,i}\,[MRed]_{i,0}}{(k_{1,i}-k_{2,i})\,(k_{3,i}-k_{2,i})}-\frac{k_{2,i}\,[MOx]_{i,0}}{(k_{2,i}-k_{3,i})}\right)\exp(-k_{2,i}t)\\ &+\left(\frac{LS\,[M]_{i,0}}{1000}+\frac{k_{2,i}\,[MOx]_{i,0}}{(k_{2,i}-k_{3,i})}\right.\\ &\left.+\frac{k_{2,i}\,k_{1,i}\,[MRed]_{i,0}}{(k_{1,i}-k_{3,i})\,(k_{2,i}-k_{3,i})}\right)\exp(-k_{3,i}t)\end{aligned} \quad (6)$$

where LS corresponds to the Liquid/Solid ratio of the experiment, and $[M]_i$ and $[M]_{i,0}$ are concentrations expressed in units of μg/L whereas $[MRed]_{i,0}$ and $[MOx]_{i,0}$ are expressed in mg/kg.

The use of seawater as the leaching liquid, the consideration of the start of the assay after 15 minutes of homogenisation (CENT/TS 14997, 2006) and the oxidation of the sediment and sediment porewater during preparation, cause the studied elements to be present in the seawater at t=0 h (i.e., $[M]_{i,0} \neq 0$). When the adsorption or precipitation process does not occur, $k_{3,i} = 0$, Eq.6 simplifies to Eq. 7:

$$\frac{LS}{1000}\left([M]_i - [M]_{i,0}\right) = \\ = [MRed]_{i,0} + [MOx]_{i,0} + \frac{k_{2.i}[MRed]_{i,0}}{k_{1,i} - k_{2.i}} \exp\left(-k_{1,i}t\right) + \\ + \left(\frac{k_{1,i}[MRed]_{i,0}}{k_{2,i} - k_{1,i}} - [MOx]_{i,0}\right) \exp\left(-k_{2,i}t\right) \quad (7)$$

The realisation of the model and the estimation of the corresponding parameters are completed using the Aspen Custom Modeler software which solves rigorous models and simultaneously estimates the parameters. The NL2SOL nonlinear least squares algorithm has been used to determine the estimated parameters. This tool minimises the weighted absolute squared error between the observed and predicted values of the measurements. When a large range of experimental values is involved in the analysis, the solver allows the user to set the weights of the measured variables to prevent a few high experimental values from dominating the residual minimisation result. In the present work, the weights were used to work with the average experimental values of each set of analysed experiments (each pH value) with the same magnitude order as the weighting criteria.

3. EXPERIMENTAL METHODS

The estuarine sediment samples were collected near the sea in a site representative of the Suances estuary (northern Spain). This estuary is part of an area that has been classified as a potential location for the implementation of Carbon Capture and Storage (CCS) techniques by the Spanish Government (BOE, 2008). This area has historically been subjected to a mixture of anthropogenic pressures, and it is classified as the highest priority site with regard to pollution. Surface sediment (0-5 cm layer) and its initial water content were collected using a pre-cleaned plastic paddle and then sieved through a 2 mm plastic mesh to remove the gravel fraction. Later, the samples were homogenised and finally frozen in plastic bags until use. The total metal content and total organic carbon of the sediment were obtained as explained in Martín-Torre et al. (2015).

A pH dependence leaching test with continuous pH-control was performed following the CEN/TS 14997 (2006) standard. However, the particle diameter, the duration of experiment and the leaching agent were modified, to better represent the potential marine acidification scenarios. The pH-static experiments were performed using a system consisting of a glass-made 2-litres jacketed vessel, a MM44 pH controller (Crison), a peristaltic pump (Ismatec) and a temperature controller (Polyscience) (Fig. 1). The MM44 pH controller, which is accurate to 0.01 pH units, uses a suitable electrode for samples with suspended solids and was calibrated against standard solutions. It is connected to the peristaltic pump that adds acid to the suspension as needed to maintain the predefined pH value. All the experiments were carried out at a constant temperature of 20ºC.

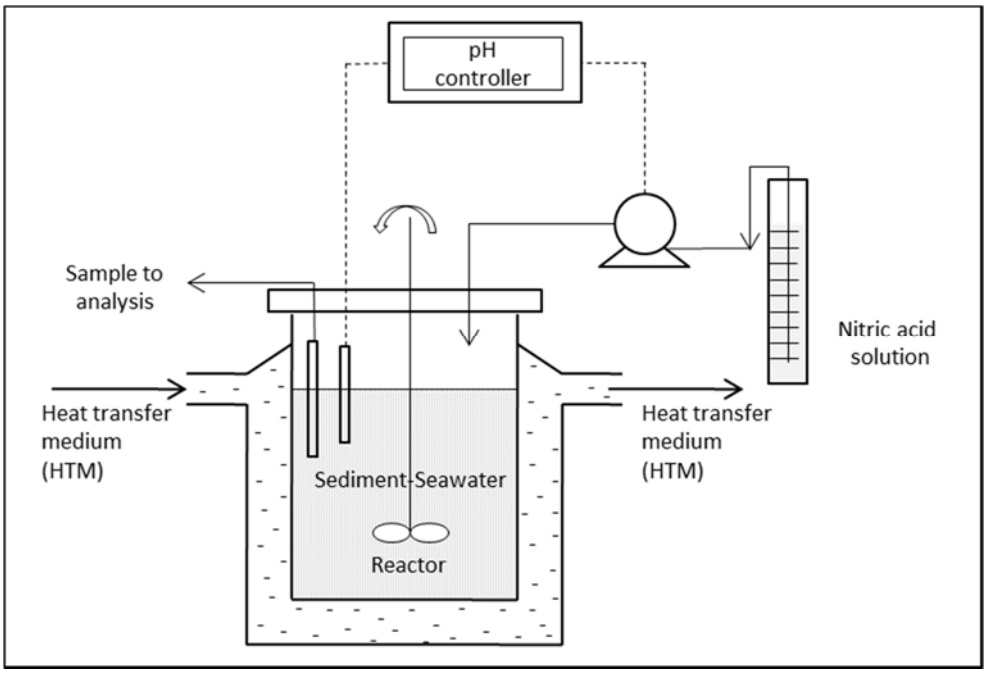


Fig. 1. Experimental equipment used in the leaching test with continuous pH-control.

The leaching liquid (seawater) and the solid (sediment) were placed in the reactor at the L/S ratio (LS) of 10, taking into account the moisture of the solid (51.26%), as recommended by the standard. Before the experiment began, the sediment and seawater were shaken for 15 minutes at the natural pH to homogenise the suspension. Because the objective of the experiment is to simulate different acidification situations without exceeding the predefined pH values (4, 5, 5.5, 6, 6.5, 7), the concentration of the nitric acid solution (0.3-5 M) used in each assay depends on the pH set point. Moreover, to maintain a constant pH throughout the assay, the hysteresis allowed in the pH controller was 0.05.

Although the standard indicates a duration of 48 hours the test performed in this study was lengthened systematically to 96 hours as a trade-off between element release and experiment duration (Cappuyns and Swennen, 2008a; Ho et al., 2012; Van Herrewegue et al., 2002). Despite this, the current experiments do not reach equilibrium in element

229 release. Therefore, the tests were lengthened and sampled until there was no addition of
230 acid in the last 24 hours of the experiment, assuming this indicated a zero release of
231 pollutant. At different times during the assay (0, 30 min, 1 h, 3 h, 6 h, 12 h, 24 h, 48 h, 72
232 h, 96 h, as well as at the time equilibrium is reached), and without interrupting the mixing,
233 a sample of the suspension was taken using a syringe. The redox potential (Eh) was
234 measured using a Basic 20 pH meter (Crison) with a special electrode for samples with
235 suspended solids.
236
237 Afterwards, each sample was filtered through a 0.45 μm pore size nitrocellulose filtration
238 membrane and acidified to analyse the concentrations of Zn, Pb, Cd, Ni, Cu, Cr and As.
239 Trace element analyses were completed using an ICP-OES Perkin Elmer Optima 3200RL
240 and an Agilent 7500CE ICP-MS using the He collision mode. Element analysis
241 calibrations were performed using reference solutions made of certified commercial
242 solutions (Inorganic Ventures). The detection limits for the elements under study (Zn, Pb,
243 Cd, Ni, Cu, Cr and As) were 10, 0.4, 0.4, 2, 2, 4 and 2 μg/L, respectively. Prior to the
244 experiments, all laboratory material was pre-cleaned, acid washed (10% HNO_3) and
245 rinsed with Milli-Q water (Direct-Q 5 UV, Merck Millipore). All leaching tests were
246 performed in duplicate.
247

248 ## 4. RESULTS

249 ### 4.1. Sediment sample and characterisation

250 The principal crystalline phases in the sediment under study are quartz, aluminium oxide,
251 calcite and dolomite (Romero et al., 2008). The concentrations of the major elements
252 (expressed as oxides) and trace elements are shown in Table 1. The organic matter content
253 expressed as Total Organic Carbon (TOC) is 4.83. The concentrations of Pb and Zn are

254 one order of magnitude higher than those of the other trace elements and are 564 and 5220
255 mg/kg, respectively.
256
257 **Table 1.** Sediment concentrations of the major elements, organic matter (expressed as
258 loss on ignition (LOI) and TOC) and trace elements.
259

Element	Content (mg/kg)	Trace element	Content (mg/kg)
Si	243316	Zn	5220
Ca	55103	Pb	564
Al	22783	Cd	12.6
Fe	16087	Ni	36
Mg	12966	Cu	48
K	7845	Cr	72
Na	5861	As	59
Ti	3602		
P	349		
Mn	232		
	LOI (%)	18.2	
	TOC (%)	4.83	

260
261 **4.2. Experimental results from the pH-static test**
262 The results obtained for the studied elements from the modified CEN/TS 14997 assay are
263 shown in Fig. 2. The release of Cd at pH>6 and Cr when pH ≠ 4 are below the detection
264 limit of the analytical equipment, so they are not shown.

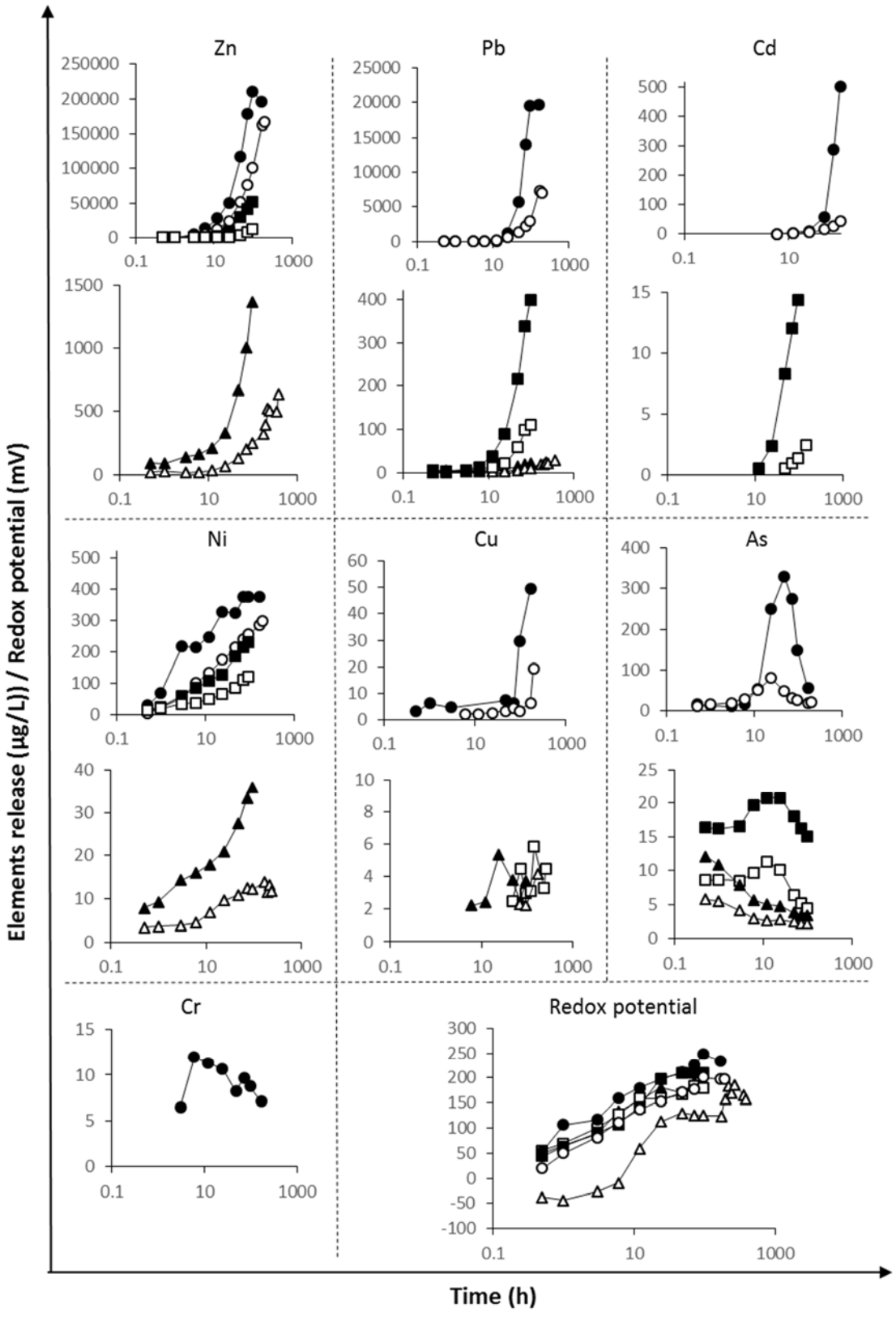


Fig. 2. Evolution of element release concentration (µg/L) and redox potential (mV) over time at different pH values: ● pH=4, ○ pH=5, ■ pH=5.5, □ pH=6, ▲ pH=6.5, △ pH=7

Different time-dependent leaching behaviours are shown in Fig. 2. There is a first pattern (Ni) in which an initial rapid release occurs and a near-equilibrium condition is reached after some hours. The rate needed to achieve the equilibrium condition depends on the reaction rate coefficients; this pattern is well-explained by the model of Schwarz et al. (1999) as well as by the model proposed in this article. In a second behaviour, there is a very slow initial release or an initial delay followed by a rapid release that decreases until equilibrium is reached. In Fig. 2, this leaching pattern is observed for Zn, Pb, Cd ($pH \leq 6$) and Cu ($pH = 4$). This initial delay could be due to the association of these metals with sulphur and the slow oxidation kinetics of the metal sulphides during the assay (Ho et al., 2012; Cappuyns and Swennen, 2008a). This oxidation process involves a speciation change, which is considered in the proposed model of the present work. The third release behaviour displays an initial rapid release followed by a maximum concentration of the element in the liquid and a subsequent decrease. This decrease, observed in the case of Cr at pH=4 and As, could be the consequence of adsorption on iron (Fe)- and aluminium (Al)-(hydr)oxides (Cappuyns and Swennen, 2008b; Martín-Torre et al., 2015).

Fig. 2 also shows the evolution of the redox potential over time for the studied pH values. A rapid increase occurs in the first six to twelve hours, depending on the pH, after which the Eh value continues to increase until thirty hours and then remains stable. In this study, similarly to Cappuyns and Swennen (2005), the evolution of the redox potential over time is as useful as the exact values, because the measured value is a mixed redox potential, rather than a true equilibrium potential, due to the different redox couples in the sediment and the slow kinetics of redox reactions (Sigg, 2000). The Eh values at $t = 0$ h and $t = 96$ h for all the studied pH values are shown in Table 2. Although the initial redox potential values are different for each pH value, the differences of the redox potential values at 0

and 96 hours decrease with pH, probably because of the decrease in the oxidation process rate. This decrease implies a slower rate of release of elements from the reduced fractions, which should oxidise before releasing the elements.

Table 2. Redox potential (mV) of the samples at t=0 h and at t=96 h.

Redox potential (mV)	pH					
	4.00	**5.00**	**5.50**	**6.00**	**6.50**	**7.00**
t = 0 h	-25.7	-58.3	-26.0	-21.5	7.0	-65.0
t = 96 h	248	201	209	180	182	144

The initial negative Eh values indicate that the sediment samples are anoxic. In most anoxic sediment, sulphides are considered the predominant solid phases controlling the concentrations of Cu, Cd, Fe, Mn, Ni, Pb and Zn. These metal sulphides might oxidise, producing oxidised sulphur species (SO_4^{2-}, S^0) and releasing the associated metal. This released metal may in turn be quickly scavenged by or co-precipitated with iron and manganese hydroxides or complexed organic matter (Simpson et al., 1998). Moreover, the oxidation of metal sulphides to S^0 or SO_4^{2-} produces the release of H^+, acidifying the medium and decreasing the pH value.

4.3. Modelling results

The experimental results shown in Fig. 2 are simulated using the proposed model, except for the release of Cu at pH ≠ 4 because an increase of the pollutant release is not observed over time. When the adsorption process is not observed, the element release is modelled using Eq. 3 because ($k_{3,i} = 0$). However, the release of Cr (pH = 4) and As is modelled using Eq. 2, considering the adsorption or precipitation process.

Initially, the released concentration of element (M) for each pH value is modelled independently. According to Eqs. 2-3, $[MRed]_{i,0}$, $[MOx]_{i,0}$, $k_{1,i}$, $k_{2,i}$ and $k_{3,i}$ (when the

element is adsorbed on the sediment) should be estimated. The estimated values of $[MRed]_{i,0}$ and $[MOx]_{i,0}$, which depend at least on the pH and the sediment oxidation level, are shown in Table 3. However, the rate coefficients $k_{1,i}$, $k_{2,i}$ and $k_{3,i}$ mainly depend on the pH and fit well to a second order polynomial equation (Fig. 3) with correlation coefficients (R^2) between 0.980 and 0.998. In the cases of Cu and Cr, only the results at the most acidic pH value (pH=4) are estimated; at more neutral pH values, their release over time does not present a clear trend or is below the detection limit. At pH=4, the estimated rate coefficients values for Cu and Cr are $k_{1,Cu} = 3.45\ 10^{-3}$ h^{-1}, $k_{2,Cu} = 3.72\ 10^{-3}$ h^{-1}, $k_{3,Cu} = 0$ h^{-1} and $k_{1,Cr} = 0$ h^{-1}, $k_{2,Cr} = 0.391$ h^{-1}, $k_{3,Cr} = 3.20\ 10^{-3}$ h^{-1}. In the case of Cu there is no adsorption process, whereas Cr release occurs very fast and no oxidation process is observed.

337 **Table 3.** Estimated values of $[MRed]_{i,0}$ and $[MOx]_{i,0}$ expressed in units of mg/kg.

338

Element (i)	pH											
	4		5		5.5		6		6.5		7	
	$[MRed]_{i,0}$	$[MOx]_{i,0}$	$[MRed]_{i,0}$	$[MOx]_{i,0}$	$[MRed]_{i,0}$	$[MOx]_{i,0}$	$[MRed]_{i,0}$	$[MOx]_{i,0}$	$[MRed]_{i,0}$	$[MOx]_{i,0}$	$[MRed]_{i,0}$	$[MOx]_{i,0}$
Zn	2110	46.1	1660	178	157	19.1	526	31.5	39.6	8.94	5.47	0.974
Pb	213	15.0	99.4	2.95	10.9	2.97	3.99	1.22	0.0122	0.474	0.384	0.0806
Cd	7.37	0	2.35	0.0462	1.01	0.198	1.05	0.0247	-	-	-	-
Ni	1.48	2.30	2.05	1.11	1.95	1.11	1.76	0.439	0.380	0.195	0.0294	0.0750
Cu	212.9	0	-	-	-	-	-	-	-	-	-	-
Cr	0.118	0	-	-	-	-	-	-	-	-	-	-
As	8.49	0	3.39	1.83	3.33	1.44	0.447	2.03	0	2.40	0	4.31

339

The rate coefficient of the oxidation and speciation change chemical reaction, $k_{1,i}$, presents a similar behaviour for all the studied pollutants except for As (Fig. 3). The values of $k_{1,i}$ for Ni and Pb are almost equal and are higher than those of Cd and Zn at the most acidic pH values and similar to $k_{1,Zn}$ when pH ≥ 6.5. However, $k_{2,i}$ presents different behaviours depending on the element. Nickel releases most rapidly: $k_{2,Ni}$ is an order of magnitude higher than the rate coefficient of Pb, the second most rapidly released. At acidic pH values, Zn is released more slowly than Cd, but the situation is the opposite when the pH is higher than 6: Zn is released more rapidly than Cd. Apparently, Arsenic is released more slowly and it is rapidly adsorbed with increasing adsorption rates when the pH increases.

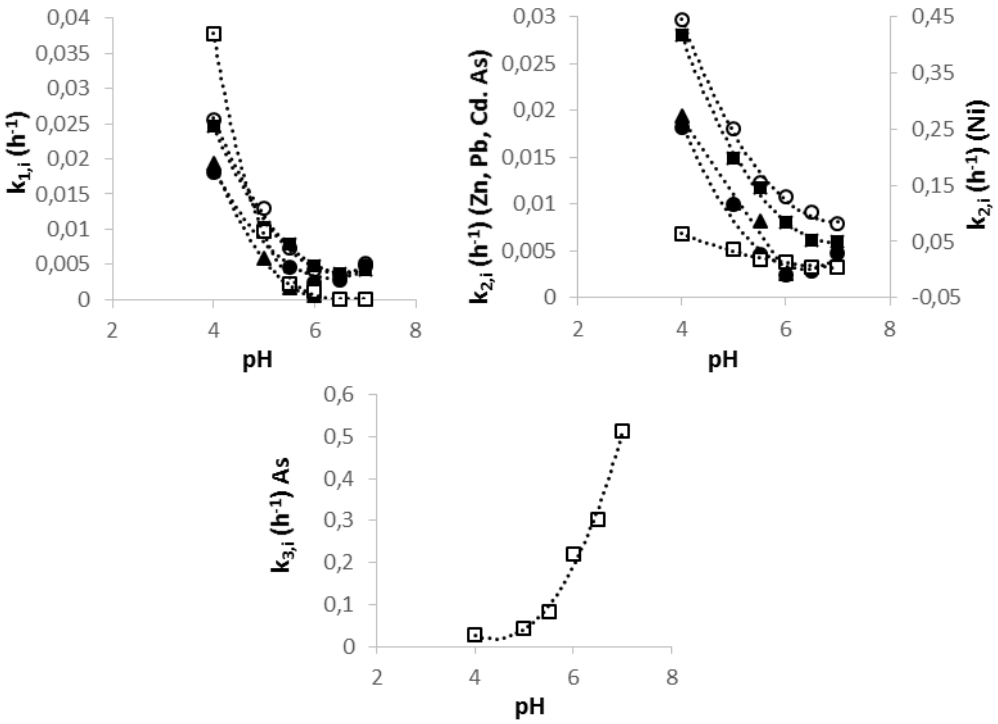


Fig. 3. Rate coefficients *vs.* pH for the studied elements: ● Zn, ■ Pb, ▲ Cd, ○ Ni, □ As. The curves fit a polynomial of second order (.....).

The good fits shown in Fig. 3 allows the introduction of a second order equation, which correlates the rate coefficients with the pH, in the mathematical equation of the proposed

357 model (Eqs. 2-3). This polynomial equation is $k_{j,i} = n_{j,i}\,pH^2 + m_{j,i}\,pH + p_{j,i}$, where
358 $n_{j,i}$, $m_{j,i}$ and $p_{j,i}$ are the coefficients of the second order equation for the pollutant i
359 involved in the chemical reaction j. The inclusion of these polynomial equations allows
360 the rate coefficients to be expressed as functions of the pH and allows estimation of the
361 polynomial coefficients taking into account the initial concentrations ($[MRed]_{i,0}$ and
362 $[MOx]_{i,0}$ from Table 3) and all the experimental results at different pH values at the same
363 time for each element. The estimated values of $n_{j,i}$, $m_{j,i}$ and $p_{j,i}$ for each element are
364 shown in Table 4. Additionally, the correlation coefficients (R^2) and relative standard
365 deviations ($\bar{\sigma}$) of the pollutant release over time, considering all the experimental results
366 at once, are shown in Table 4.
367
368 **Table 4.** Coefficient values of the kinetic constants as a function of pH, adjusted to a
369 polynomial of order two: $k_{j,i} = n_{j,i}\,pH^2 + m_{j,i}\,pH + p_{j,i}$, for pollutant i and reaction j.
370 The correlation coefficients (R^2) and average standard deviation ($\bar{\sigma}$) parameters for the
371 relation between the experimental and simulated released concentrations using the
372 proposed model are shown.
373

Pollutant i/ reaction j		**Zn**	**Pb**	**Cd**	**Ni**	**As**
Oxidation Reaction	$\mathbf{n_{1,i}}$	$3.23\ 10^{-3}$	$3.32\ 10^{-3}$	$3.70\ 10^{-3}$	$3.32\ 10^{-3}$	$1.05\ 10^{-2}$
	$\mathbf{m_{1,i}}$	$-4.21\ 10^{-2}$	$-4.31\ 10^{-2}$	$-4.57\ 10^{-2}$	$4.350\ 10^{-2}$	-0.122
	$\mathbf{p_{1,i}}$	0.143	0.143	0.142	0.147	0.359
Release Reaction	$\mathbf{n_{2,i}}$	$1.33\ 10^{-2}$	$2.63\ 10^{-3}$	0	$8.20\ 10^{-3}$	$6.28\ 10^{-3}$
	$\mathbf{m_{2,i}}$	-0.168	$-3.57\ 10^{-2}$	$-7.79\ 10^{-3}$	-0.206	$9.03\ 10^{-2}$
	$\mathbf{p_{2,i}}$	0.540	0.128	$5.01\ 10^{-2}$	1.11	0.328
Adsorption Reaction	$\mathbf{n_{3,i}}$	-	-	-	-	$5.93\ 10^{-2}$
	$\mathbf{m_{3,i}}$	-	-	-	-	-0.515
	$\mathbf{p_{3,i}}$	-	-	-	-	1.14
Statistical Parameters	$\mathbf{R^2}$	0.991	0.971	0.949	0.992	0.990
	$\bar{\sigma}$	0.191	0.536	0.476	0.109	0.198

374

375 Figs. 4 and 5 show the experimental and modelled pollutant release over the first 48 hours
376 (Fig. 4) and at longer times of the assay (Fig. 5), where near-equilibrium conditions are
377 achieved in most of the cases (Fig. 5). The modelled curves fit well to the experimental
378 results when an initial delay is observed except in the case of Pb and Cd at pH=4. The fit
379 is also poor in the case of Cu at pH=4 at 72 h (Fig. 5). Fig. 6a is the parity plot obtained
380 for the validation of the proposed model in terms of the released metal concentrations at
381 any time and pH value (n=308). The correlation coefficient (R^2) for this comparison is
382 0.992, which indicates a good correspondence between the experimental and predicted
383 metal concentrations. A good fit of the proposed model is also confirmed by the fact that
384 80.2% of the experimental data lie within a model relative error of ±20%; however, larger
385 deviations were noticed (Fig. 6b) in the case of Zn, Pb and Cd at pH = 4. In these cases,
386 the experimental results indicate a longer metal release delay that is not explained by the
387 proposed model. The longer release time could be due to the displacement reactions, a
388 consequence of the different solubility products. For example, iron (Fe) and manganese
389 (Mn) monosulphides are partially soluble in water, with increasing solubility when the
390 pH is reduced, whereas the sulphides of the studied metals from the highest to the lowest
391 solubility, NiS, ZnS, CdS, PbS and CuS are less soluble than Fe and Mn monosulphides
392 (Di Toro et al., 1990). The sulphur ions present in the medium because of the dissolution
393 of Fe and Mn monosulphides favour the precipitation of dissolved Ni, Zn, Cd, Pb and Cu
394 ions as a consequence of displacement reactions (Eq. 8).
395

$$M^{2+}(aq) + FeS(s) \rightleftarrows MS(s) + Fe^{2+}(aq) \quad (8)$$

396

where M= Ni, Zn, Pb, Cd or Cu. The effect of these displacement reactions is more pronounced at acidic pH values because of the higher solubility. At higher pH values (pH>4), the oxidation process is the main reason for the initial delay.

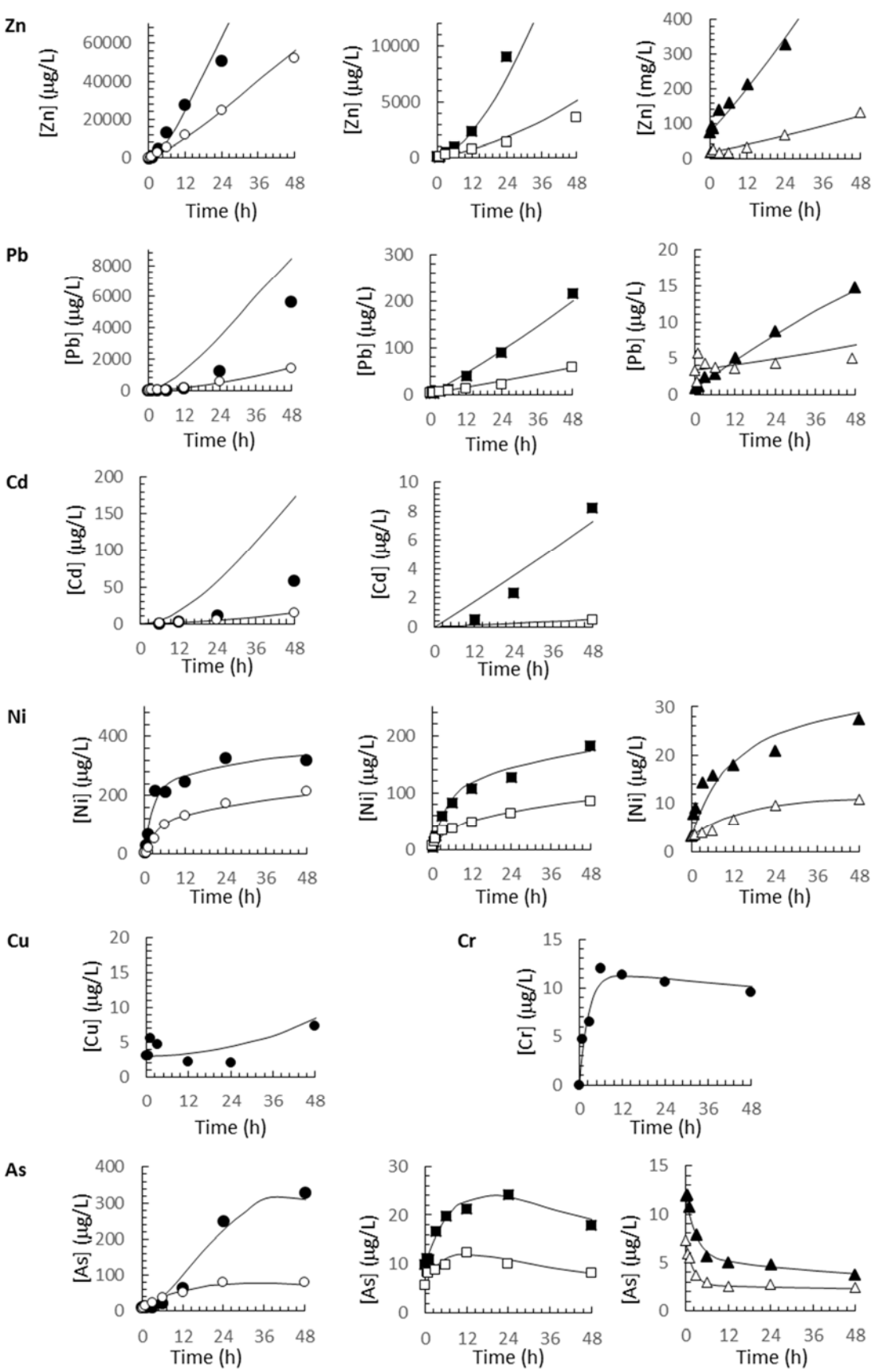


Fig. 4. Pollutant release at short times at different pH values. Experimental data: ● pH=4, ○ pH=5, ■ pH=5.5, □ pH=6, ▲ pH=6.5, △ pH=7; — Simulated results using the proposed model (Eqs. 6 and 7)

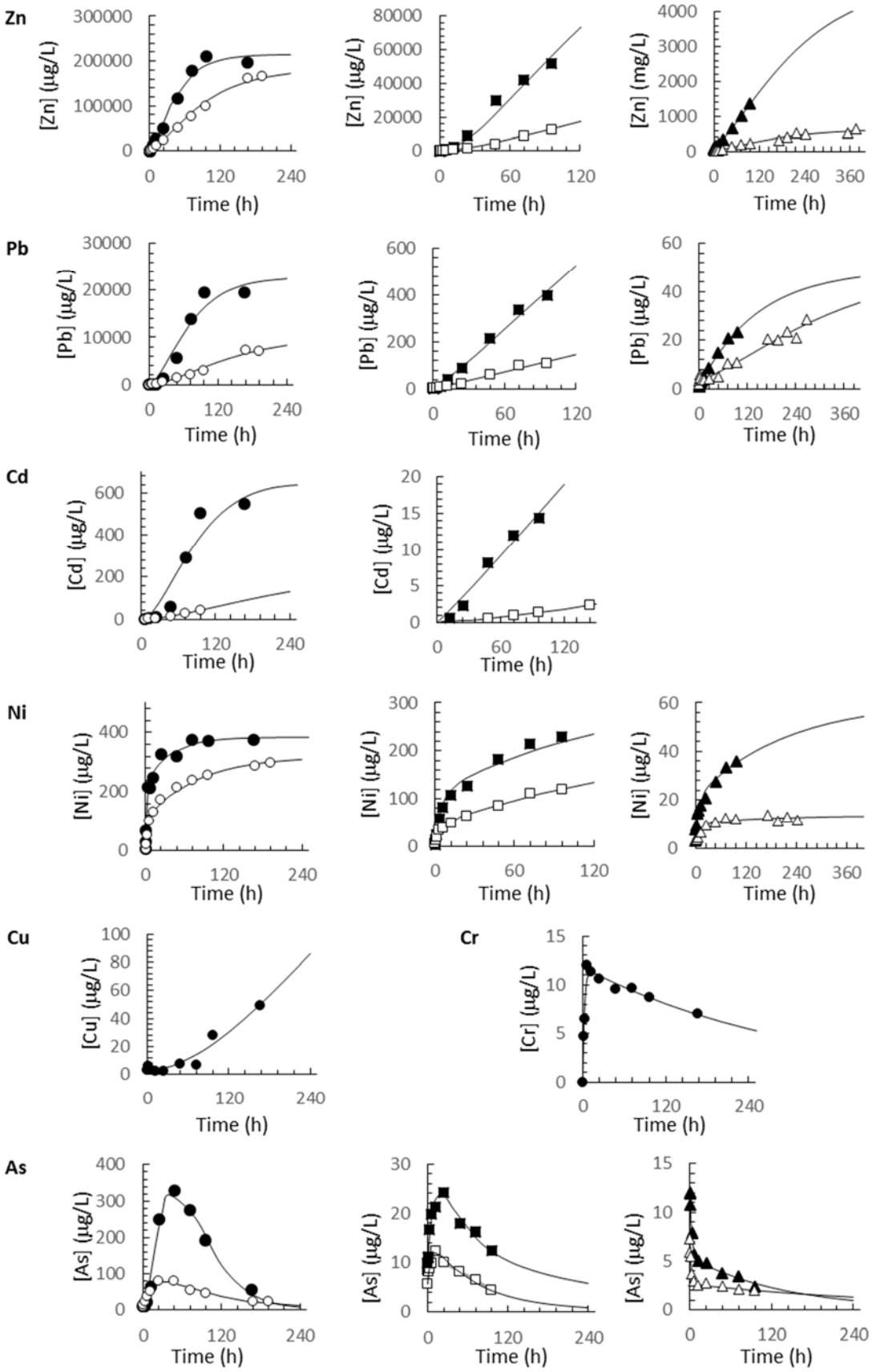


Fig. 5. Pollutant release over time at different pH values. Experimental data: ● pH=4, ○ pH=5, ■ pH=5.5, □ pH=6, ▲ pH=6.5, △ pH=7; ⎯ Simulated results using the proposed model (Eqs. 6 and 7)

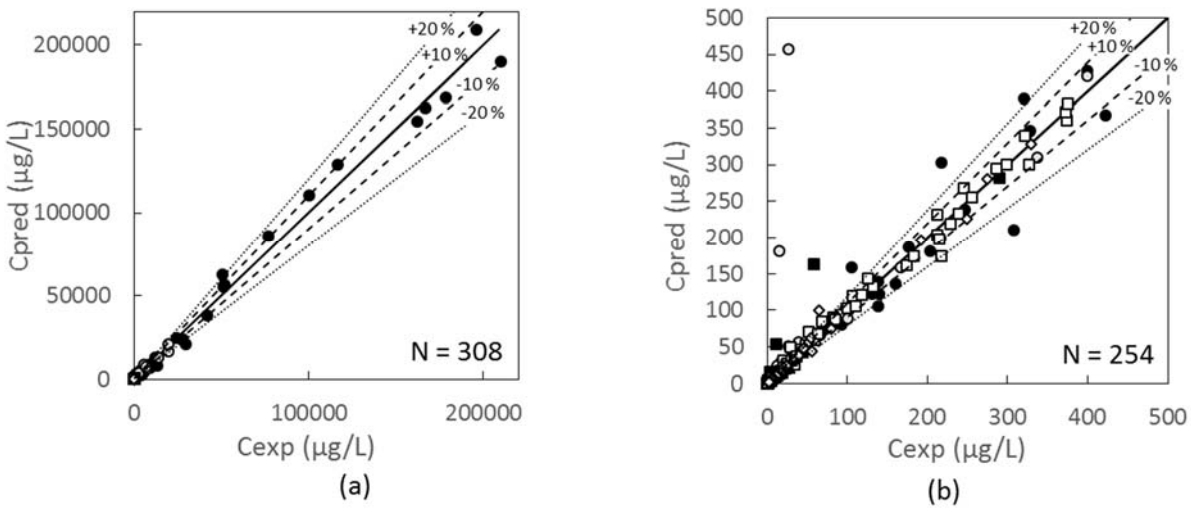
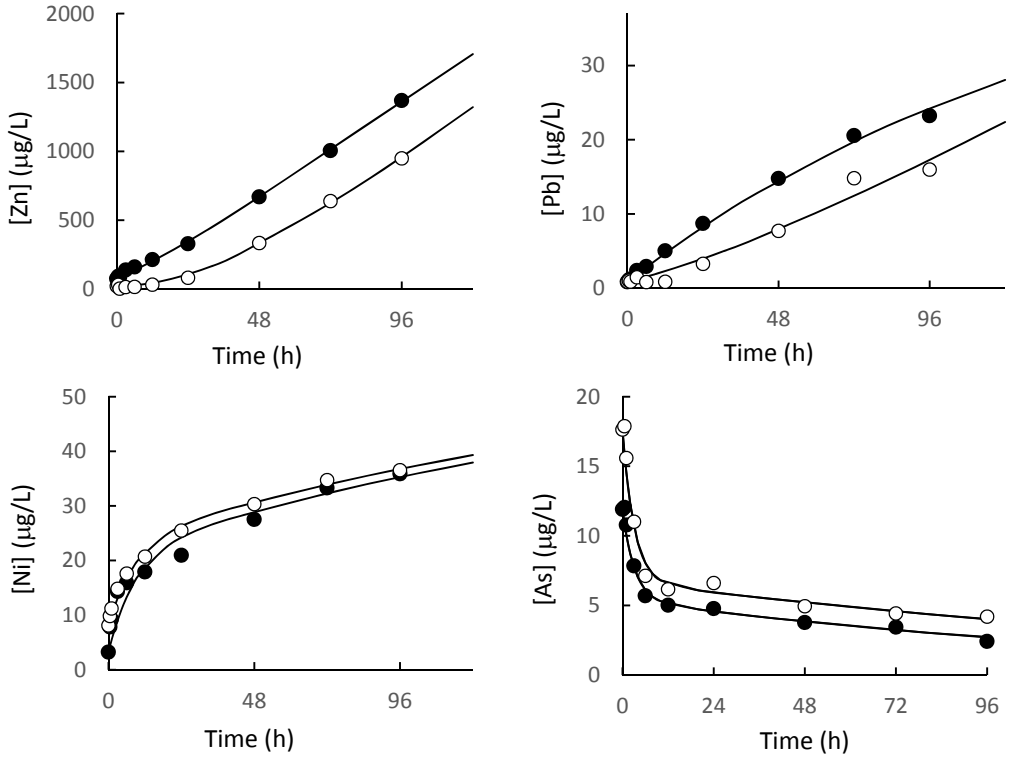


Fig. 6. Parity plot of the metal concentrations from the experiment (Cexp) and predicted by the proposed model (Cpred) of ● Zn, ○ Pb, ■ Cd, □ Ni, ▲ Cu, △ Cr and ◇ As. - - - indicates ±10% model relative error, and ..... indicates ±20% model relative error. The numbers of fitted data points are N= 308 (Fig. 6a), and N= 254 (Fig. 6b).

The delay in the release of elements is compared with the redox potential values at t=0 h. The Eh values are similar at pH= 4 and 5.5 (-25.67 mV and -26.00 mV, respectively), therefore element release presents a similar delay of approximately 6-12 hours or slightly longer in the cases of Cd (approximately 12 -24 hours) and Cu (approximately 24-36 hours). Arsenic at pH=4 also presents a delay of 6-10 hours. At pH=5, the initial redox potential is -58.33 mV, so there is a slightly longer delay (approximately 12 hours) in the case of Zn, Pb and Cd. When the pH=6 and the Eh is -21.00 mV, the delays of Zn and Pb are 12-24 hours, possibly due to the decrease of the kinetics rate. There is no delay when pH=6.5 because the initial sediment was quite oxidised (Eh=7.00 mV). At pH=7 the redox potential is lowest (-65.00 mV) which causes an important delay in the trace metal release, especially in the case of Pb (24 hours). Moreover, in the cases of Zn and Pb, a slight adsorption appears at short times probably due to the metal adsorption consequence of the displacement reactions (Eq. 5).

552 The influence of the oxidation state of the sediment is studied by comparing the Zn, Pb,
553 Ni and As results at pH=6.5 with the results from another assay at the same pH value but
554 carried out with reduced sediment (initial redox potential of -148 mV). From the
555 experimental release of the considered elements and by using the proposed model,
556 $[MRed]_0$ and $[Mox]_0$ are estimated. The rate coefficients depend on the pH and not on
557 the oxidation level of the sediment, so the previous estimated values are considered (Table
558 4). In Fig. 7, the experimental and simulated element releases from the reduced and
559 oxidised sediments over time are presented. The statistical parameters R^2 (between 0.928
560 - 0.999) and relative standard deviation (between 0.17 - 0.004) shown in Table 5 indicate
561 that the experimental values are very close to the predicted ones. In Table 5, the estimated
562 values of $[MRed]_0$ and $[Mox]_0$ are shown for the oxidised and reduced sediments; the
563 values for the oxidised sediment are the same as those in Table 3. For all the studied
564 elements, $[MRed]_0$ is higher than $[Mox]_0$ when the reduced sediment is used, as
565 expected. The table also lists the maximum element concentration that can be released,
566 calculated as $[MRed]_0 + [Mox]_0 + [M]_0$; it is higher when the initial sediment is
567 reduced. The lower element release from the oxidised sediment could be due to adsorption
568 of pollutants during the oxidation process (Cappuyns and Swennen, 2005). In many types
569 of sediment is unclear which areas are oxic and anoxic and both phases could coexist,
570 especially at depths up to 10 centimetres (Burdige, 1993; Simpson et al., 2000;
571 Williamson et al., 1999). Hence, the model proposed in this work allows a more reliable
572 simulation of real situations because is valid for any initial sediment oxidation level.
573



574

575

576

577 **Fig. 7.** Zn, Pb, Cd and As release over time at pH=6.5 using sediments at different
578 levels of oxidation. ● Experimental data using oxidised sediment;
579 ○ Experimental data using reduced sediment; — Simulated results using the proposed
580 model.

Table 5. Estimated values of $[MRed]_{i,0}$ and $[MOx]_{i,0}$ for the oxidised and reduced sediments, initial values of the pollutant concentrations (experimental value t = 0) and maximum contaminant concentrations in mg / kg. The R^2 and $\bar{\sigma}$ parameters of the relation between the experimental and simulated released concentrations using the proposed model are also shown.

	Zn		**Pb**		**Ni**		**As**	
	Oxidised	Reduced	Oxidised	Reduced	Oxidised	Reduced	Oxidised	Reduced
$\mathbf{[MRed]_{i,0}}$	39.6	52.7	0.0122	1.05	0.380	0.385	0	0.153
$\mathbf{[MOx]_{i,0}}$	8.94	0	0.474	0.156	0.195	0.151	2.40	1.76
$\mathbf{[M]_0}$	0.756	0.213	$8.26\ 10^{-3}$	$8.43\ 10^{-3}$	0.0322	0.0912		
$\mathbf{[MRed]_{i,0}+[MOx]_{i,0}+[M]_0}$	49.3	52.9	0.494	1.21	0.607	0.627	2.40	3.97
$\mathbf{R^2}$	0.999	0.998	0.996	0.967	0.928	0.997	0.982	0.977
$\bar{\sigma}$	0.00414	0.0536	0.0678	0.173	0.167	0.0323	0.0772	0.0956

5. CONCLUSIONS

This work presents a kinetic model of the evolution of Zn, Pb, Cd, Ni, Cu, Cr and As concentrations over time when polluted sediment is totally mixed with inorganic acid-acidified seawater under semibatch leaching tests with continuous pH control at pH values of 4, 5, 5.5, 6, 6.5 and 7. The model considers three reactions in series: (i) the oxidation reaction of the reduced fraction to take into account the speciation change over time, (ii) the metal release of the oxidised fraction to the bulk dissolution and (iii) the adsorption or precipitation after the element release.

The maximum concentrations of each element that can be released from the reduced and oxidised fractions of the sediment as well as the rate coefficients of the kinetic reactions are estimated by applying the proposed model to the experimental results. These maximum concentrations depend on the pH and the sediment oxidation level, whereas the rate coefficients only depend on the pH and fit well to a second order equation as a function of the pH. Using the Aspen Custom Modeler software, the model parameters have been estimated.

The parity plot shows a good agreement between the experimental and modelled concentration values and confirms that the developed model can be applied to predict the element release from polluted sediment under acidic conditions at different and constant pH values. In the cases of Cu at pH≠4**,** the proposed model cannot be applied because the time-dependent leaching does not present a clear trend. Additionally, the model has been applied successfully to the mobility of Zn, Pb, Ni and As at pH = 6.5 using two sediments with different levels of oxidation; the validity of the model could be further verified by working at a wider range of pH values with variable oxidation states.

The proposed model explains all the behaviour of the pollutant release from contaminated sediments or soils. Unlike the previous model of Schwarz et al. (1999), the proposed model predicts reasonably well the metal mobility delay at short times for Zn, Pb, Cd and Cu and the adsorption or precipitation process after an initial rapid release (As and Cr). The obtained model results would be useful as evidence in seawater acidification risk assessments and they predict the release of Zn, Pb, Cd, Ni, Cu, Cr and As for scenarios in which seawater acidified by inorganic acid at a constant pH is mixing with recently polluted sediment.

Acknowledgements

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